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Report Title

EXCITED ELECTRONIC STATE DECOMPOSITION MECHANISMS AND DYNAMICS OF NITRAMINE ENERGETIC MATERIALS AND MODEL SYSTEMS

ABSTRACT

The energetic materials RDX, HMX, and CL-20 are studied in the gas phase by mass spectroscopy, optical wavelength resolved and time resolved spectroscopic techniques. We learn that NO is the first product of the dissociation of these molecules excited to their first electronic excited singlet states. The NO appears at less than 100 fs following the excitation pulse. A number of cyclic and non cyclic nitramine model systems are studied in parallel with the energetic materials and, which NO is their first decomposition product from their excited electronic states, it appears with a very different internal energy distribution. We suggest a number of possible general ideas for improving the energy yield from energetic materials.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

M. Greenfield, Y. Q. Guo, and E. R. Bernstein, "Ultrafast Photodissociation Dynamics of HMX/RDX From the Excited Electronic States Via Femtosecond Laser Pump-Probe Techniques," Chem. Phys. Lett., 430, 277 (2006).

Y. Q. Guo, M. Greenfield, and E. R. Bernstein, "Decomposition of Nitramine Energetic Materials in Excited Electronic States: RDX and HMX," J. Chem. Phys., 122, 244310 (2005).

184. E. R. Bernstein, "Role of Excited Electronic States in the Decomposition of Energetic Materials," in Overviews of Recent Research on Energetic Materials, D. Thompson, T. Brill, R. Shaw, Eds. (World Scientific, New Jersey, 2005), p. 161.

Number of Papers published in peer-reviewed journals: 3.00

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2. UV Excited Electronic State Decomposition of Energetic Materials and Model Systems using fs Laser Spectroscopy.
3. UV Single Photon Dissociation of Furazan Based Energetic Materials: DAAF.

ACS:

4. UV Excited Electronic State Decomposition of the Energetic Materials HMX and RDX using ns and fs Laser Spectroscopy.

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Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	
Margo Greenfield	0.00	No
Ataner Bhattacharyn	0.50	No
FTE Equivalent:	0.50	
Total Number:	2	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	
Yuanging Guo	1.00	No
FTE Equivalent:	1.00	
Total Number:	1	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Elliot R. Bernstein	0.10	No
FTE Equivalent:	0.10	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PHDs

<u>NAME</u>	
Margo Greenfield	No
Total Number:	1

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

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EXCITED ELECTRONIC STATE DECOMPOSITION MECHANISMS AND DYNAMICS OF NITRAMINE ENERGETIC MATERIALS AND MODEL SYSTEMS

Energetic materials play an important role in aeronautics, the weapon industry, and the propellant industry due to their broad applications as explosives and fuels. RDX (1,3,5-trinitrohexahydro-s-triazine), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), and CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane) are compounds which contain high energy density (J/cm^3) or (J/g). Although RDX and HMX have been studied extensively over the past several decades, a complete understanding of their decomposition mechanisms and dynamics is unknown. This work describes the novel approach taken to assist in the overall understanding of the decomposition of these energetic materials, namely their gas phase single molecule excited state decomposition.

Excited electronic states can be generated by shock and compression and therefore play an important role in the initiation/ decomposition of RDX, HMX, and CL-20. Energy (ns lasers) and time resolved (fs lasers) UV-photodissociation experiments have been performed to elucidate the mechanisms and dynamics of gas phase energetic material decomposition from excited electronic states. Time of flight mass spectroscopy (TOFMS), laser induced fluorescence (LIF), and pump-probe experiments performed on three energetic materials, as well as five model systems, illustrate the unique behavior of energetic materials.

TOFMS UV photodissociation (ns) experiments of gas phase RDX, HMX, and CL-20 generate the NO molecule as the initial decomposition product. Four different

vibronic transitions of the initial decomposition product, the NO molecule, are observed: $A^2\Sigma(v'=0) \leftarrow X^2\Pi(v''=0,1,2,3)$. Simulations of the rovibronic intensities for the $A \leftarrow X$ transitions demonstrate that NO dissociated from RDX, HMX, and CL-20 is rotationally cold (~ 20 K) and vibrationally hot (~ 1800 K). Conversely, experiments on the five model systems (nitromethane, dimethylnitramine, nitropyrrolidine, nitropiperidine and dinitropiperazine) produce rotationally hot and vibrationally cold NO spectra.

LIF experiments are performed to rule out the possible decomposition product OH, generated along with NO, perhaps from the suggested HONO elimination mechanism. The OH radical is not observed in the fluorescence experiments, indicating the HONO decomposition intermediate is not an important pathway for the excited electronic state decomposition of cyclic nitramines.

The NO molecule is also employed to measure the dynamics of the excited state decomposition. A 226 nm, 180 fs light pulse is utilized to photodissociate the gas phase systems. Stable ion states of DMNA and nitropyrrolidine are observed while the energetic materials and remaining model systems present the NO molecule as the only observed product. Pump-probe transients of the resonant $A \leftarrow X$ (0-0) transition of the NO molecule show a constant signal indicating these materials decompose faster than the time duration of the 226 nm laser light. Comparison of NO from the three energetic materials to NO from NO_2 gas generated by a 180 fs light pulse at 226 nm indicates that NO_2 is not an intermediate product of the excited electronic state photodissociation of RDX, HMX, or CL-20.

Two possible excited state decomposition mechanisms are suggested for the three energetic materials. The first mechanism involves a dissociative excited electronic state

in which the nitramine moieties (CNNO_2) in the electronically excited energetic material isomerize (CNONO) and further dissociate. In the second possible decomposition mechanism the electronically excited molecules undergo internal conversion to very highly excited (~ 5 eV of vibrational energy) vibrational states of their ground electronic state. Once in the ground state, isomerization of the nitramine moieties occurs and the material further decomposes. Computational results together with the experimental results indicate the energetic materials decompose according to the second mechanism, relaxation to the ground state, while the model systems follow the excited electronic state decomposition pathway. An additional path in which the $-\text{NO}_2$ moiety loses an O atom, become linear with the CN attachment, and then NO is released, is also consistent with experimental observations but is, as yet, not supported by calculations.

The keys to generating better cyclic nitramine energetic materials would then be to enhance the propensity to form $S_1 - S_0$ conical intersections, improve $S_1 - S_0$ Franck-Condon factors for internal conversion near the S_1 zero point level, and to enhance the S_0 density of vibronic states at high S_0 vibrational energy. Additionally, one would like to generate NO with less internal vibrational excitation, so altering the NONO vibrational excitation in the dissociation process could be important. These ideas would suggest that more flexible cyclic nitramines, with increased internal degrees of freedom, might be useful to explore for new energetic systems. Perhaps larger ring structures along the lines of CL-20 might be useful compounds to explore.

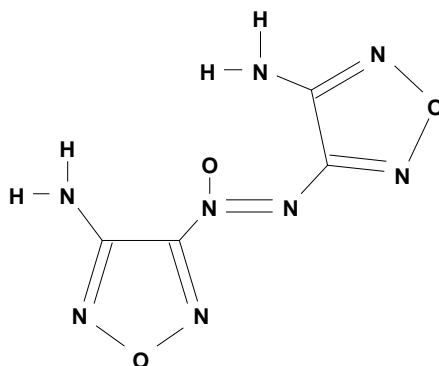
Future Direction with New Systems

Current UV photodissociation experiments on the energetic materials RDX, HMX, and CL-20 suggest the most probable excited electronic state decomposition mechanism is due to an internal conversion of the excited molecules to very highly excited vibrational states of their ground electronic state. If this is indeed true, production of better cyclic nitramine materials would require a S_1 - S_0 conical intersection, an improved S_1 - S_0 Franck-Condon overlap for internal conversion near the S_1 zero point level, and an enhanced S_0 density of vibronic states at high S_0 vibrational energy. Compounds that are more likely to have these characteristics are flexible cyclic nitramines with increased internal degrees of freedom.

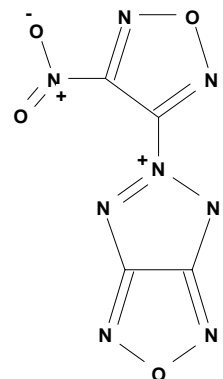
CL-20 is thought of as a bridging system to more compact and crowded multi-ring systems and as an entrée into the high nitrogen content species shown in Figure 1 and Figure 2. Studies presented in this work show that electronically excited gas phase CL-20 behaves similarly to electronically excited gas phase RDX and HMX. The suggested decomposition mechanism of CL-20 is internal conversion to very highly excited vibrational states of its electronic ground state. Due to its caged structure CL-20 is probably not as flexible as the longer chained high nitrogen containing species BTATZ or NOTO. If internal conversion plays an important role in the behavior of an energetic material and it is dependent upon the flexibility of the structure, BTATZ and NOTO should give products with high vibrational temperatures. Studying the UV excited state decomposition of these energetic materials by utilizing ns spectroscopy to determine their decomposition products (NH_2 , NH , NO , CH , N_2O) and the rotational and vibrational temperatures associated with them will give information as to how they decompose as a

function of vibrational and electronic state. Time resolved fs spectroscopy experiments on BTATZ or NOTO might determine the mechanism and dynamics for the initial stages of their decomposition as a function of their electronic and vibrational states.

Furazan Based Energetic Materials

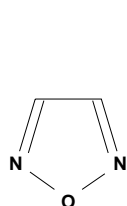


DAAF, diaminoazofurazan

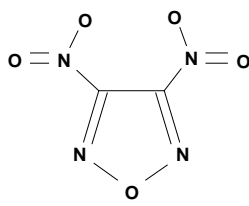


NOTO, 5-[4-nitro-(1,2,5)oxadiazolyl]-5H-[1,2,3]triazolo[4,5-c][1,2,5]oxadiazole

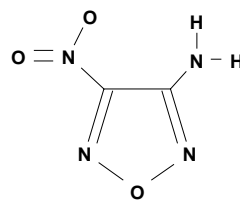
Model systems of Furazan Based Energetic Materials



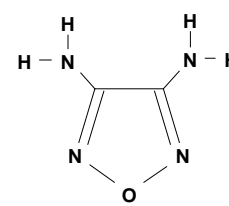
Furazan



3,4-dinitrofurazan



3-amino-4-nitrofurazan



3,4-diaminofurazan

Figure 1. Furazan based energetic materials and model systems

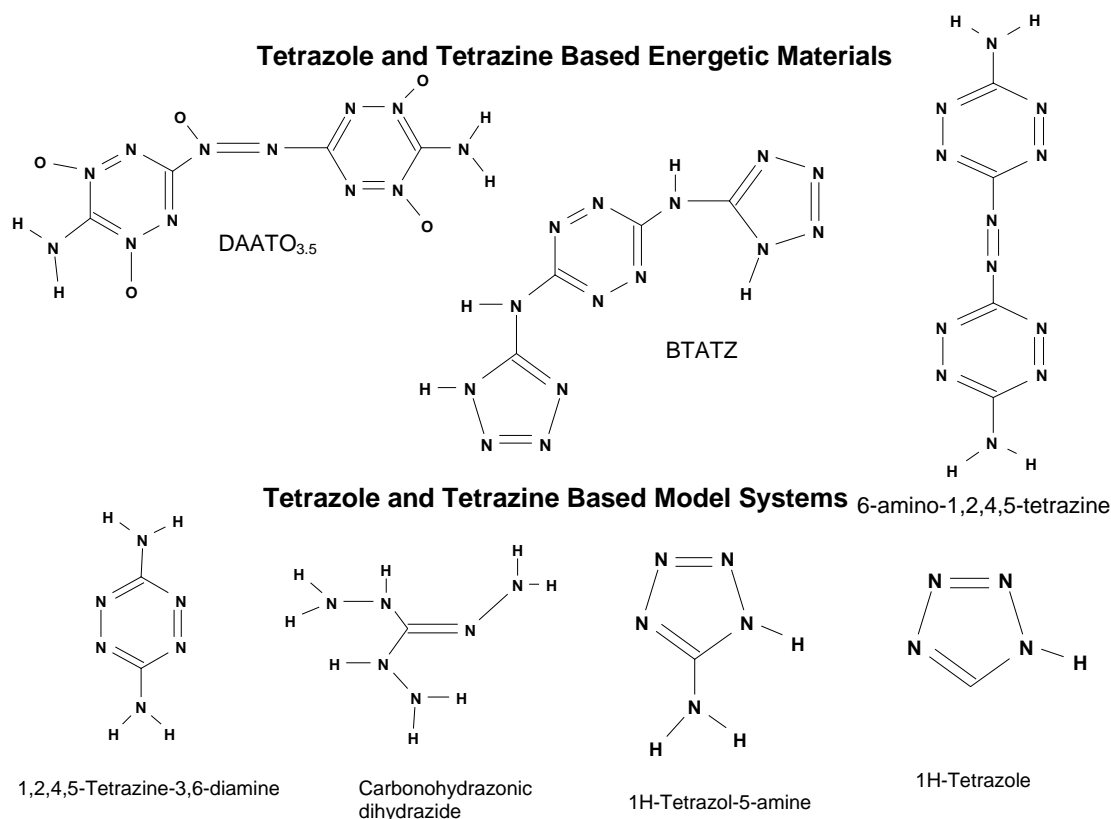


Figure 2. Tetrazole and tetrazine based energetic materials and model systems

Initial UV excited state decomposition studies on the furazan based high nitrogen energetic material DAAF show the initial decomposition product, the NO molecule, is not as vibrationally hot as NO from RDX and HMX. This suggests that, although DAAF is larger in structure than HMX and RDX and would seemingly give decomposition products with an enhanced S_0 density of vibronic states at high S_0 vibrational energy, the rigidity of the N=N double bond between the furazan like moieties possibly reduced its flexibility and internal degrees of freedom thereby decreasing the internal conversion of the excited state molecules to the highly excited vibrational states of the ground electronic state. Further investigations into the importance of structural make-up (material, orientation, bonding type, flexibility, etc) of the energetic materials will allow

for better understanding of its efficiency and will help in exploring possibilities for new energetic materials.

There are many non-energetic furazan, tetrazole and tetrazine based systems that can be investigated as model systems. The model systems are appealing on many levels. First, the systems are smaller so analyzing the experimental results might be easier. Second, elucidating the true nature as to why some compounds are “energetic” while similar ones are not must arise through a comparison of the decomposition mechanisms and dynamics of the model systems to the energetic materials.

Finally, including calculational and experimental efforts for these new systems will allow for better understanding of the excited state decomposition mechanisms. Calculations will suggest new species and pathways to explore for the experiments while the experiments will provide direction for the calculations, so that a complete picture of the decomposition mechanism will be established. The ideal energetic material would lead to small molecule gas phase products that are internally cold (low T_{rot} and T_{vib}) with very high T_{trans} . These future studies will help understand how this can be achieved and may aid in the generation of such stable molecular energetic species.